PATENT SPECIFICATION

758,538

Index at acceptance :—Classes 1(1), A3A1(A:X), A3C2; and 2(3), B4B, C3A14A(3B:7B).

COMPLETE SPECIFICATION

Method and Apparatus for Temperature Control of Catalytic Chemical Reactions

I, HERBERT PETER AUGUST GROLL, a Swedish subject, of Kyrkogatan 1a, Molndal Sweden, do hereby declare the invention, for which I pray that a patent may be granted to
5 me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with a method and apparatus for temperature control of
10 catalytic chemical reactions with relatively high heats of reaction, more specifically with providing effective means for transferring the heat of reaction between the reacting mixture and a suitable heating or cooling medium. My
15 invention allows the temperature of the zone of reaction over its whole length to be held constant to a degree that heretofore was considered impossible.

Most catalysts demand a limited tempera-
20 ture interval for successful operation. If the temperature is too low the reaction rate becomes insufficient, if it is too high the catalyst is damaged or destroyed, or undesirable side-reactions occur. It is however not
25 always necessary or desirable to operate under such conditions that the temperature in the reaction zone is constant over the whole length of this zone. A certain limited temperature gradient may in some cases be desirable. For
30 example, in certain cases it may be advisable to apply a relatively low reaction temperature for the initial stages in the reactor in order to prevent overheating and consequent deterioration of the catalyst and to raise the tempera-
35 ture at the end of the reaction zone so that the last traces are converted at a sufficiently high reaction rate although the concentration of the substances to be reacted becomes quite low. On the other hand, in other cases it may
40 be desirable to carry out the bulk of the reaction at a comparatively high temperature and to lower the temperature towards the end of the reaction passage so that a more complete conversion can take place.

45 In order to maintain essentially isothermic reaction conditions it is always necessary that the whole heat of reaction be transferred out of the reaction space, i.e. through the walls of the reaction vessel. It is to be understood that

in this specification and in the ensuing claims 50 the term "walls of the reactor" includes not only the outside walls of the apparatus but also all kinds of cooling walls which may be arranged inside the reactor, e.g. cooling tubes inserted into the reactor proper or the walls 55 of the catalyst tubes which are surrounded by the cooling medium. If the heat of reaction per unit of operating time is named W and the heat transferred per unit operating time is named q we have a first condition for an iso- 60 thermic reaction course the equation.

$$1) \qquad W = -q$$

This condition, however, while guaranteeing a sufficient amount of cooling does not state anything about the rate at which the 65 heat is transferred at any given spot of the whole length (L) of the reactor. If we assume that the reactor has the shape of tubes or channels through which the reagents are passed and the heating or cooling medium is 70 outside the tubewalls the contact time t becomes a simple function of L and we find the other condition for an isothermic reaction course

$$2) \qquad \frac{dW}{dL} = -\frac{dq}{dL} \qquad 75$$

(I wish to emphasize that a tubular form of the reactor is not at all necessary for carrying my invention to practice. Other reactor shapes may be used equally successfully).

While condition (1) only assumes that the 80 temperature at the end of the reaction zone is the same as that at its beginning it does not take into consideration great local deviations from the desired temperature during the passage of the reagents through the tube. 85 Condition (2) if adhered to prevents any such deviations and should, if it can be fulfilled, provide ideal reaction conditions.

It is well known that endothermic reactions are much easier to control than exothermic 90 ones. The former show the great advantage that they tend to stabilize any upset temperature conditions automatically. This is due to the fact that the rate of reaction, rising and falling with the temperature, automatically 95 and effectively adjusts the rate of heat con-

sumption to the rate of heat supply. In other words, the thermal steady state equilibrium is stable. In contrast to this an exothermic reaction must be held at an unstable thermal equilibrium by rigid outside control. With inadequate cooling the temperature, the reaction rate, and the rate of heat formation rise so that the temperature is driven up in a viscious circle which causes the reaction to " go wild ". The opposite happens when the rate of cooling is too rapid so that the reaction " dies ".

From the viewpoint of difficulty of control, exothermic reactions may be classified in several classes:—

CLASS I

Those reactions which hardly need any temperature control because they occur with good yields at such high temperatures, within such a wide temperature interval, and on a heat stable catalyst that no external cooling is necessary at the reaction zone. The combustion of ammonia to nitric oxide is a typical example for this class. The upper allowable temperature limit is in this case controlled by the proportion between ammonia and air, and by the temperature to which the air is preheated.

CLASS II

Those reactions which owing to their nature and to the nature of the catalyst available must be carried out within a temperature interval at which the chemical equilibrium does not allow a complete reaction to occur so that a great part of the reagents leave the reactor unchanged and must be recirculated. Thus if the reaction temperature rises owing to incomplete heat removal the equilibrium becomes still more unfavourable, thus preventing further reaction unless a lower temperature is restored by adequate cooling. This is a very convenient self-regulating effect which facilitates operation tremendously with this reaction type and does not allow the reaction to go wild. Ammonia synthesis is a typical example of this class in which the recirculation mentioned above is applied. Another example is the water gas reaction for the conversion of carbon monoxide to carbon dioxide and hydrogen. In this case the gas leaving the convertor should contain as little as possible unconverted carbon monoxide. Therefore a plurality of catalyst layers are used, the gas being cooled between layers. The yields per pass and the capacity of a given apparatus does, in any case, depend entirely upon the efficiency of heat removal.

CLASS III

Reactions which occur on particularly temperature-sensitive catalysts and/or which are inclined to change over to undesirable side-reactions. This class is very frequent in organic chemistry and includes a wide variety of reactions. Typical examples in the order of increasing difficulty of control are: hydrogenations, the oxo-process, methanol and isobutanol synthesis, partial hydrogenations, selective oxidations, the Fischer-Tropsch process, oxidation of naphthalene to phthalic anhydride and of ethylene to ethylene oxide. The last 3 are generally considered so difficult to control that only special measures such as thermostatic agitated salt baths, liquid evaporator systems, internal cooling, or operation under great dilution with recycle-gas are deemed adequate.

My invention can be carried into practice with great advantage for all reactions of class 2 and 3, while it can be considered unnecessary for class 1. My invention is based upon the perception that it is possible to adjust the rate of cooling in suitably designed apparatus so that it follows perfectly the conditions set out by equations (1) and (2) without having to resort to extraordinary and expensive thermostatic evaporating baths or the like. As a matter of fact thermostatic evaporating baths are not as effective as they generally are considered. Keeping the bath temperature constant throughout the bulk of the liquid does not prevent the temperature in the reaction passage proper from rising considerably above the temperature of the cooling liquid, especially at such points where the reaction occurs at its highest rate.

The rate of reaction depends upon the concentration of the reagents in the reaction zone, the rate constant k which generally is a function of the temperature, the order of the reaction, and the catalyst activity. The order of the reaction concerned depends upon its mechanism which in many cases is not fully understood, especially if the reaction occurs upon a solid catalyst. The rate can, however, be determined by measurements and the order of reaction can thus be ascertained. Experience shows that most catalytic reactions are of first or second order. As the mechanism may be complicated and the rate may be determined by more than one elementary process occurring simultaneously, so called mixed orders such as between zero and 1st or between 1st and 2nd order, may result. On the basis of these determined and/or calculated values the rate of conversion at any desired moment of the contact time can be calculated and a satisfactory function derived for the rate of heat formation in any section of the reactor. In other words the values for

$$\frac{dW}{dL}$$

can be expressed as a function of L by an equation or by a curve.

This function is, for any reaction of the type

3) $$\frac{dW}{dL} = \frac{Q}{v} F(c_a, c_b \ldots)$$

Q=molar heat of reaction

v=linear velocity of flow of the reactants

c_a, c_b, etc.=concentration of reagents at any spot of the reactor. These are functions of L

a, b, etc.=initial concentrations of reagents

F(...), f(...), φ(...) express functions in the well known manner.

The function $F(c_a, c_b ...)$ is generally of a type in which the term

$$e^{-f(L)}$$

is of decisive importance, while the linear velocity v itself may be a function of L if the reaction is accompanied by an expansion or contraction:—

$$v=\phi(L)$$

In the first approximation v can be regarded as constant and in many cases where the practical concentrations are sufficiently far apart from the equilibrium concentrations at the reaction temperature applied, the necessary equations can easily be derived from the well known rate equations. For instance the equation for a first order reaction is

4) $$\frac{dW}{dL}=-k_1\frac{Q}{v} a\, e^{-k_1\frac{L}{v}}$$

k_1=velocity constant for the first order reaction under the reaction conditions chosen.

For an ideal second order reaction the equation becomes somewhat more involved:—

5) $$\frac{dW}{dL}=\frac{Qk_2\frac{a}{b}(b-a)^2 e^{k_2\frac{L}{v}(a-b)}}{v\left(1-\frac{a}{b}e^{k_2\frac{L}{v}(a-b)}\right)^2}$$

In practice, empirical equations often must be resorted to because the conditions become too involved for theoretical deduction. The type of the equation is, however, always that of equation (3) with $e^{-f(L)}$ as decisive term.

The typical shape of a curve representing this type of equation is seen in Figure 1a, which shows the value of $\frac{dW}{dL}$ as a function of L. In the same figure another function $\frac{dq}{dL}$ is drawn which represents the amount of heat removed from the reactor at any point of its length. Completely isothermic conditions are obtained if the values of $\frac{dq}{dL}$ and $\frac{dW}{dL}$ assume equal absolute magnitude, however with opposite sign. In this case which is shown in Figure 1a the two curves are exactly symmetrical to each other with the abscissa as axis of symmetry.

I have now found that the cooling method which lends itself best to a perfect adaption to the rate required by the reaction rate function consists of cooling with a cooling medium which flows concurrently with and parallel to the flow of the reacting mixture. The rate equations for the heat taken up by a flowing cooling medium from an isothermic heat source per unit of operating time are:—

6) $$q=Cn(\theta_1-\theta_2)$$

7) $$\frac{dq}{dL}=\kappa(\theta'-\theta_1)e^{-\frac{\kappa D\pi L}{n.C}}$$

The symbols in these equations mean:—

κ=heat transfer constant in a given apparatus design

q=heat taken up per unit of operating time

L=tube length

D=tube diameter

C=medium molar heat capacity of cooling medium

θ'=reaction temperature

θ=temperature of the cooling medium

θ_1=temperature of the cooling medium entering the apparatus

θ_2=temperature of the cooling medium leaving the apparatus

n=number of moles of cooling medium per unit of operating time.

The heat of radiation has not been considered in the above equation. In cases in which radiation becomes so high that it cannot be neglected the function becomes more complicated without changing its general character.

The values for q and $\frac{dq}{dL}$ should according to equations (1) and (2) be equal to the negative values of W and $\frac{dW}{dL}$ if perfect temperature control is to be achieved.

The complete equations read as follows:—

8) $$-Cn(\theta_1-\theta_2)=W$$

I.

9) $$\kappa(\theta'-\theta_1)e^{-\frac{\kappa D\pi L}{n.C}}=-\frac{Qk_2\frac{a}{b}(b-a)^2 e^{k_2\frac{L}{v}(a-b)}}{v\left(1-\frac{a}{b}e^{k_2\frac{L}{v}(a-b)}\right)^2}$$

In equation 9 both sides are of the *e*-function type. It is obvious that the value of the right side of the equation is determined by the nature of the reaction and of the catalyst (Q
5 and k_2), the concentration of the reagents (*a* and *b*), the gas velocity (*v*), and the dimensions of the apparatus (L). The value of the left side, on the other hand, is determined by design factors of the apparatus (D, L and κ)
10 and the nature of the cooling medium (C and κ). The designer of the apparatus should obviously choose these parameters within suitable limits in considerations to the nature and velocity of the reaction (represented chiefly
15 by the right side of the equation). This is necessary in order to make it possible that both sides of the equation can become equal to each other. Under this prerequisite of design which makes the application of my invention possible with-
20 out, however, being part of the invention, the balance of the equations 8 and 9 under operating conditions can at any time under the operation be changed by controlling only the parameters *n* and θ_1. These control parameters,
25 however, represent the flow velocity of the cooling medium and its temperature at the entrance to the apparatus.

In order to achieve this control I arrange the concurrent parallel flow of the cooling medium
30 in such a manner that the rate of flow of the cooling medium *n* and the temperature of the cooling medium entering the cooling passage of the reactor θ_1, can be controlled independently of each other, instan-
35 taneously, and effectively over the ranges of temperature and flow rate required. Thus my invention in its broadest aspect can be defined as a method for carrying out exothermic, preferably heterogeneous, catalytic re-
40 actions, of flowing homogeneous gaseous or liquid reactants, the heat generated by the reaction being removed by indirect cooling with a cooling medium flowing concurrently with the reaction mixture, characterized by
45 the fact that the reaction temperature along the flow path of the reaction mixture is maintained at predetermined values by controlling (i) the temperature of admission of the cooling medium and (ii) the throughput of cooling
50 medium per unit time, both these factors being controlled independently of each other and independently of the amount of reaction mixture passing through the reaction zone per unit time. By controlling the cooling in this way
55 the perfect balance between the heat of reaction and the heat removal shown by the 2 symmetrical curves in Figure 1a aforesaid can be maintained at any time during the operation of the apparatus. In Figure 1b there is shown
60 the temperature increase of the cooling medium which occurs in removing the heat at

the rate of the $\dfrac{dq}{dL}$ function shown in Figure 1a.

It is seen that the temperature θ of the cooling

medium asymptatically approached the opti-
65 mum reaction temperature of the reaction in question. The reaction temperature θ' becomes isothermic as also shown in Figure 1b.

One preferred way of achieving the temperature control described is to recirculate the cool-
70 ing medium, e.g. by means of a pump, a blower, or an injector, to pass the cooling medium through an effective cooling device with sufficient capacity for cooling the recycled cooling medium at the highest flow rate to the
75 lowest temperature required, and to provide a bypass of the hot medium, said bypass being regulatable instantaneously by a valve or a flap. If air or cooling water is used directly as cooling medium no cooling of the recycle stream is necessary and it is only necessary to provide
80 a recycle line for hot cooling medium in order to regulate the temperature of the cooling medium entering the system with the speed and effectiveness necessary.

A further preferred method of carrying my
85 invention into practice is to provide automatic control to both the temperature and flow regulations of the cooling medium. The control points of this automatic control are:—

A) The region of the temperature maximum
90 in the reagents passage through the reactor in the immediate neighbourhood of the entrance of the cooling medium to the cooling passage through the reactor. I provide this point with a suitable temperature control device con-
95 nected to an instrument of conventional design which automatically regulates the temperature of the cooling medium entering the cooling passage of the reactor.

B) The exit point of the reacted gas mixture
100 from the catalyst zone is controlled by a similar device connected to an automatic control instrument which regulates the rate of flow of the cooling medium to the cooling passage of the reactor.
105

I prefer to adjust the regulating instrument controlled by point (A) during the initial stages of the lifetime of a catalyst to maximum temperature which the catalyst tolerates without deterioration by overheating. The regulating
110 instrument (B) is set to a temperature somewhat above the lower temperature limit necessary for a satisfactory rate of reaction. In special cases, particularly the end of the lifetime of a catalyst charge, I may prefer to set
115 this instrument near the upper allowed limit.

In the latter stages of the operating period I may increase or decrease the controlled temperatures of these points and/or I may move
120 the control point A further into the reactor. Which of these measures are best suited in order to achieve the best results depends so much upon the nature of reaction, the type of catalyst used, and the cause of its gradual
125 deterioration e.g. whether this is due to poisoning and/or sintering or other changes of its active surface, that it is impossible to recom-

mend the best measures beforehand. It is best to determine the optimal operating modus within the known limits empirically.

I may also move the point of entry of the cooling medium further into the reactor during the course of the operating period so as to avoid undesirable excessive cooling of such parts of the catalyst as may become less active.

I may achieve this protection against undue cooling by protruding a protecting device, e.g. an isolating shield, gradually or periodically in between the flow of the cooling medium and such parts of the catalyst that need protection.

I may even provide internal heating inside the catalyst in the portion immediately following the entrance of the reagents in order to safeguard the reaction against "dying" accidentally by too violent cooling. A preferred method for carrying my invention into practice is to provide an entry or initiating zone filled with catalyst which is not or not effectively cooled. This method is especially useful in such cases, where it appears undesirable or impossible to preheat the reagent mixture fully up to the preferred reaction temperature, because of an inherent danger of decomposition.

In the entry zone the reagents react over the catalyst more slowly than at the usual reaction temperature. The heat of reaction heats up the reaction mixture to the preferred temperature. Cooling should begin immediately at the spot where the proper reaction temperature is reached. I may provide means for regulating the length of the entry zone by protruding shields or the like as was described above.

Another particularly useful method for putting my invention into practice is to use the reaction mixture or alternatively one or a plurality of constituents thereof as cooling medium.

E.g. in carrying out ammonia synthesis I may pass the mixture of nitrogen and hydrogen or only nitrogen under the synthesis pressure through the cooling passage of the reactor in such a way, that the rate of flow and the temperature of the cooling gas are regulated independently from one another and independently from the rate of throughput of the reaction mixture through the catalyst proper.

In the synthesis of phthalic anhydride by oxidation of naphthalene with air I may prefer to use air directly for cooling the reaction tubes in which the catalyst is placed or I may place the catalyst in the interspace between the tubes and pass the air through the cooling tubes spaced evenly throughout the catalyst bed. In order to provide a better distribution of the cooling gas and a better heat transfer I may provide the cooling tubes with centre rods held in position by spiders or by spiral fins. These rods increase the gas velocity and the flow resistance, thereby facilitating even distribution of gas between all the tubes and enhancing the heat transfer rate. For the same purpose I may fill the cooling tubes or the cooling space around the catalyst tubes with a packing. I may prefer to use a packing material with a high heat conductivity e.g. balls or chips of metal such as aluminium. The latter method is particularly useful for achieving a high coefficient of heat transfer to the cooling gas in such cases where this appears desirable.

One preferred feature of my invention is to ensure the parallel flow of the cooling medium with respect to that of the reaction mixture by providing plates or fins parallel to the direction of the flow in order to prevent interference of heat convection with the direction of the flow.

When applying fixed bed catalysts at high throughput rates it is customary to let the reaction mixture pass through the catalyst bed in a downward direction in order to prevent undesirable "dancing" of the catalyst which may be mechanically destroyed thereby. If the cooling medium is passed through the interspace between the catalyst tubes in a downward direction as is necessary for carrying my invention into practice in this particular case, heat convection might interfere with the direction of the flow and undesirable eddies may develop. In this case the application of directional fins or the like becomes a very useful feature of my invention. I may also use for the same purpose a method of packing the interspace with a solid packing material essentially as described. This packing increases the flow more evenly over the whole cross section of the cooling passage.

I may further provide convenient means for preventing gas or vapour lock in the cooling passage when applying a downward flow of a liquid cooling medium. For instance I may build the cooling passage of the reactor according to the principle of communicating vessels. If the flow resistance in the cooling passage demands a high differential pressure I may provide gas vent valves at the top of the cooling passage. These valves may be automatically operated by floats or the like.

I may further provide means for utilizing the heat of reaction. If this cannot be taken up completely in heating up the entering reagent mixture to the reaction temperature desired, I may provide waste heat boilers, economizers, etc.

Application for my invention is not confined to operation with fixed bed catalysts. I may use it with particular advantage in combination with the so called "fixed fluidized bed" type, i.e. with little carry over of catalyst in the gas leaving the reactor. In this case the parallel upward flow of the reacting mixture in the reactor and of the cooling medium in the cooling passages is particularly easy to accomplish because the longitudinal temperature gradient of the cooling medium does not tend to upset the even flow of the cooling medium by undesirable convection.

The application of my invention results in considerable technical and economic advantages, of which the following are the most outstanding ones:—

I prefer to make the difference between the reaction temperature and the temperature of the incoming cooling medium $(\theta' - \theta_1)$ as great as possible, that is to say so great that a sufficient amount of heat is removed from the zone of the most violent reaction without, however, cooling the catalyst too vigorously. Thus I may in certain cases use temperature differences greater than 100° C. This method allows to apply a rate of flow (n) of the cooling medium which is as low as possible, i.e. just enough to exert sufficient cooling at the end of the reaction zone. This saving of cooling medium and/or of pumping energy is a special advantage of my invention.

Another advantage of my invention is that I may use very long reactors contrary to common practice. For example in the production of phthalic anhydride reactors with many thousands of narrow tubes filled with catalysts are used which are at the most about 6 feet long. I prefer to use tube lengths of more than 20 feet, and I may even use tubes which are as long as 50 feet or longer. In these tubes the reaction gas velocity becomes extremely high so that the heat transport from the catalyst to the tube walls becomes extremely favourable so that no local hot spots can occur. Therefore, I may choose tubes with very much greater diameter than those which are commonly used. This fact, coupled with greater length of the reactor, obviously gives me the great advantage of having to apply only a much lower number of tubes in a reactor of given capacity, so that the work and the material necessary for constructing the reactor are very considerably reduced.

The invention will be described in further detail with reference to the specific embodiments shown in the drawings. The embodiments are given by way of illustration and not limitation.

Figures 2 and 3 show two typical examples of apparatus for carrying out exothermic reactions according to the method of my invention. In the apparatus shown in Figure 2 the reaction passage 1 is an extended tube surrounded by a cooling jacket. The reaction mixture enters the heat exchanger 3 through the line 2 in which it is warmed up by heat exchange with the reacted mixture leaving the reaction passage. From the heat exchanger 3 the reaction mixture passes through line 4 to the entrance 5 of the reaction mixture into the reaction passage. The first section 6 of the reaction passage 1 is the entry or initiating zone for the reaction, which is adjustable as will be described later.

The reacted mixture leaves the reaction passage at the point 7 and passes through the line 8 to the heat exchanger 3 and the discharge line 9. The circulation of the cooling agent through the jacket 10 is effected by the pump 11. The discharge line 12 from this pump leads to the valve 13 which regulates the amount of cooling agent entering the cooling jacket 10 at the point 15 through the line 14. The cooling agent leaves the cooling jacket 10 at the point 16 and passes through line 17 to the heat exchanger 18 in which the heat taken up by the cooling agent can be utilized in any convenient manner, e.g. the heat exchanger 18 may be a waste heat boiler for generating steam. The spent cooling agent is discharged from the heat exchanger 18 through line 19. It is also possible to recirculate the cooling agent to the system through the line 20 which leads to the suction line 21 of the pump 11.

A bypass is provided between line 17 mentioned above and the suction line 21 of pump 11. This bypass consists of lines 22 and 24 and the regulating valve 23 which regulates the temperature of the cooling agent. In the case described in Figure 2 the regulating valve 23 is a simple throttle which closes when the temperature becomes too high. The valve 23 allows, therefore, a variation of the amount of warm cooling agent admixed to the cool cooling agent which is admitted to the suction side of the pump either through line 21 which supplies fresh cooling agent or through the line 20 through which the cooling agent cooled down in heat exchanger 18 may be recirculated.

The automatic control of the regulating valve 23 is achieved by a thermo-regulating device 25 which is arranged immediately after the said entry zone 6 and can be adjusted by the sliding jacket 26 which insulates a portion of the reaction passage from the cooling jacket. The sliding jacket may consist of heat insulating material and/or may be provided with a heating coil in order to compensate for heat losses. The thermo-regulating device 25 also slides in order to be adjustable to the correct position relative to the end of the entry zone 6. The regulating impulse from the thermo-regulator 25 is transferred over the line 28 to a relay 29 which operates the valve 23 via the connection 30. By this arrangement the proportion of warm and cooled cooling agent in the mixture entering the cooling agent pump 11 is regulated according to the temperature measured at the location of the thermo-regulator 25.

A similar thermo-regulating device 27 is arranged at the exit end of the reaction passage. The regulating impulse are transferred over the line 31 to the relay 32 which via the connection 33 operates the valve 13. This valve regulates the flow rate of the cooling agent to the reactor automatically according to the temperature measured at the exit end of the reactor. The regulating valve 13 opens when the temperature at the location of the thermo-regulator 27 becomes too high and it closes if the tem-

perature becomes too low, thus increasing or decreasing the flow rate of the cooling agent.

The thermo-regulating devices may be of any known or conventional construction and merely comprises thermostatic control devices. When it is stated herein and in the claims that the thermo-regulating devices are arranged at certain positions in the reaction passages, as for example, at the entrance and exit ends of the passages, it is of course, understood that there is meant thereby that the temperature-sensitive portion of the thermo-regulating device is arranged at the position indicated.

The apparatus for carrying out exothermic reactions which is shown in Figure 3 is of another type in which a plurality of cooling passages 10a are inserted into a comparatively large reaction passage 1a. The conditions for heat transfer from every point of the reaction passage to the nearest cooling tube are therefore essentially the same as if the reaction passage were divided into the same number of single passages as corresponds to the number interspaces between the cooling passages. The flow of the reaction mixture proper is in this example only indicated symbolically by the entrance 5a and the exit 7a. (The plant may, however, comprise heat exchangers for pre-heating the reaction mixture and for utilizing the heat of the reacted mixture. In simple cases one heat exchanger may suffice for warming up the reaction mixture by counter current with the reacted mixture in the same manner as shown in Figure 2 in which the heat exchanger 3 is provided for this purpose).

In this example the cooling agent is completely circulated by the pump 11a placed near the exit 16a from the lower cooling agent header. The pump 11a pumps the cooling agent through the line 17a to the heat exchanger 18a where it is cooled by a secondary cooling medium e.g. air or cooling water. This secondary cooling medium is supplied through line 34 and its flow rate is regulated by the regulating valve 23a. It flows through line 35 to the shell of the heat exchanger 18a and is discharged through line 36. The valve 23a which varies the flow rate of the secondary cooling medium thus regulates the temperature of the circulating cooling agent. The latter, cooled down to the temperature desired, leaves the heat exchanger 18a through line 12a. The flow rate of the circulating cooling agent is regulated by the regulating valve 13a which allows the cooling medium to flow through line 14a at the rate desired to the sliding header 38 which distributes it to the insulated tubes 39 in the header. In these tubes the cooling agent passes to the cooling agent entrances 15a to the cooling agent passages 10a. These passages are provided with displacer rods 37 in order to increase the linear velocity of the cooling agent and to prevent convection currents.

The automatic regulation for the valves 23a and 13a is based on the same principle as shown in Figure 2: The sliding thermo-regulating device 25a arranged near the entrance of the reagents to the reaction chamber is situated after the entry zone 6a. In Figure 3 this entry zone practically does not exist at all because the header 38 is shown drawn up into its highest position. This header bears the insulated tubes 39, the thermo-regulating device 25a, the cooling agent entrances 15a, and the rods 37. If and when a longer induction zone becomes desirable the header is lowered so that the elements 39, 15a and 37 protrude further into the cooling passages 10a. In this manner that part of the reaction passages, which is protected from being cooled down by the cooling agent, can be considerably extended during the operation period which is given by the life time of the catalyst. This extension allows protection from undue cooling at that zone of the catalyst layer which in most cases gradually becomes inactive by poisoning or the like. The thermo-regulating device 25a acts over the line 28a upon the relay 29a which in turn operates the regulating valve 23a over the connection 30a. In this manner the temperature of the cooling agent is regulated by the thermo-regulating device 25 and serves to control the temperature in the zone of the highest conversion where the thermo-regulating device 25a is located. The thermo-regulating device 27a located near the exit of the reacted mixture from the reaction passage acts over the line 31a upon the relay 32a which in turn operates the regulating valve 13a by means of the connection 33a. In this manner the flow rate of the cooling agent is regulated by the thermo-regulating device 27a and this flow rate serves to control the catalyst temperature at the exit end of the reaction passage.

The application of my invention does not preclude the application of other known methods and/or devices for facilitating the control of the reaction temperature. Thus I may recycle part of the reacted gases to the reactor thereby diluting the reagents, or I may use inert gases or vapours for diluting the reagents or I may use other means for reducing the intensity of heat development in the reaction zone together with and independently of the application of my invention described above.

What I claim is:—

1. A method for carrying out exothermic, preferably heterogeneous, catalytic reactions of flowing homogeneous gaseous or liquid reactants, the heat generated by the reaction being removed by indirect cooling with a cooling medium flowing concurrently with the reaction mixture, characterized by the fact that the reaction temperature along the flow path of the reaction mixture is maintained at predetermined values by controlling (i) the temperature of admission of the cooling medium and (ii) the throughput of cooling medium per unit time, both these factors being controlled independently of each other and independ-

dently of the amount of reaction mixture passing through the reaction zone per unit time.

2. A method as claimed in Claim 1, characterised by the fact that the control of the temperature of the cooling medium is carried out in dependence of the temperature prevailing in the neighbourhood of the inlet where the reactants enter the reaction zone.

3. A method as claimed in Claim 2, characterised by the fact that the control of the temperature of the cooling medium is carried out automatically by means of a temperature-controlled device provided in the neighbourhood of the inlet where the reactants enter the reaction zone.

4. A method as claimed in Claim 2 or 3, characterised by the fact that an initial zone which is not cooled or is wholly or partially shielded from the cooling is provided between the inlet where the reactants enter the reaction zone and that portion of the reaction zone whose temperature is used for controlling the temperature of the cooling medium, the temperature of the reactants in said initial zone rising to the desired optimum temperature.

5. A method as claimed in any of the preceding claims, characterised by the fact that the control of the flow rate of the cooling medium is carried out in dependence of the temperature prevailing in the neighbourhood of the outlet where the reactants leave the reaction zone.

6. A method as claimed in Claim 5, characterised by the fact that the control of the flow rate of the cooling medium is carried out automatically by means of a temperature-controlled device provided in the neighbourhood of the outlet for the reactants.

7. A method as claimed in any of the preceding claims, characterised by the fact that the temperatures of the cooling medium entering into heat exchange contact with the reactant, and the rate of flow in the cooling medium, are independently controlled to maintain a maximum initial temperature differential between the cooling medium and reactant.

8. A method as claimed in any of the preceding claims, characterised by the fact that the cooling medium is recycled.

9. A method as claimed in Claim 8, characterized by the fact that the cooling medium to be recycled is subjected to controllable cooling.

10. A method as claimed in Claim 9, characterized by the fact that only a portion of the cooling medium to be recycled is subjected to controllable cooling.

11. A method as claimed in any of the preceding claims, characterised by employing for the cooling operation a gaseous medium, especially the gaseous reactants which are in this manner preheated to a temperature that is suitable for the catalytic reaction.

12. Apparatus for carrying out exothermic reactions according to the method claimed in any of Claims 5 to 11, comprising a reaction vessel adapted to contain a catalyst through which the reactants are adapted to flow, a container for the cooling medium which latter is adapted to flow in contact with the wall of the 70 reaction vessel and in a direction generally parallel with the flow of the reactants, primary thermally responsive means responding to temperature changes in the reaction vessel adjacent to the inlet of the reaction vessel, said primary 75 thermally responsive means being in operative association with means for controlling the temperature of the cooling medium entering the container, secondary thermally responsive means responding to temperature changes in 80 the reaction vessel adjacent to the outlet of the reaction vessel, said secondary thermally responsive means being in operative association with means for controlling the volume of cooling medium adapted to flow into 85 the container per unit time.

13. Apparatus as claimed in Claim 12, characterised by the provision of a reaction initiating zone in said reaction vessel between the inlet thereof and said primary thermally respon- 90 sive means, the catalyst in said initiating zone being internally heated or protected against cooling, or at least against excessive cooling, the boundary between said initiating zone and the reaction zone proper of said reaction vessel 95 being positioned at a region longitudinally of the reaction vessel where the proper reaction temperature is reached.

14. Apparatus as claimed in Claim 13, characterised in that the catalyst in said reaction 100 initiating zone is mechanically isolated against the cooling effect of said cooling medium.

15. Apparatus as claimed in Claim 14, characterised by shielding or screening means interposed between the cooling surfaces and said 105 reaction initiating zone.

16. Apparatus as claimed in Claim 15, characterised in that said shielding or screening means is adjustable lengthwise of the reaction vessel, thereby to elongate or shift forward 110 said initiating zone when the effectiveness in the original initiating zone has been decreased.

17. Apparatus as claimed in Claim 16, characterised in that also said primary thermally 115 responsive means is adjustable lengthwise of reaction vessel.

18. Apparatus as claimed in any of Claims 12 to 17, characterised in that said means for controlling the temperature of the cooling 120 medium entering the container comprises adjustable valve means controlled by said primary thermally responsive means and means for recycling a portion of the cooling medium after passage through the apparatus to said 125 variable valve means and back to the apparatus.

19. Apparatus as claimed in any of Claims 12 to 18, characterised in that means for passing the cooling medium through the apparatus 130

include a heat exchanger and means for re-
cycling cooling medium from the container in
the apparatus through the heat exchanger back
to that said container, said means for con-
5 trolling the temperature of the cooling medium
including variable valve means controlled by
said primary thermally responsive means,
means being provided for passing a second
cooling medium through said adjustable valve
10 means through said heat exchanger for
indirect heat exchange contact with the first
mentioned cooling medium.

20. A method for carrying out exothermic
catalytically accelerated reactions in a flowing
15 gaseous or liquid phase, substantially as herein-
before described with reference to the appa-

ratus shown in Figure 2 or 3 of the accom-
panying drawings.

21. Apparatus for carrying out exothermic
catalytically accelerated reactions in a flowing 20
gaseous or liquid phase substantially as herein-
before described with reference to and as
shown in Figure 2 or 3 of the accompanying
drawings.

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Fig. 1a.

Fig. 1b.

758,538 COMPLETE SPECIFICATION

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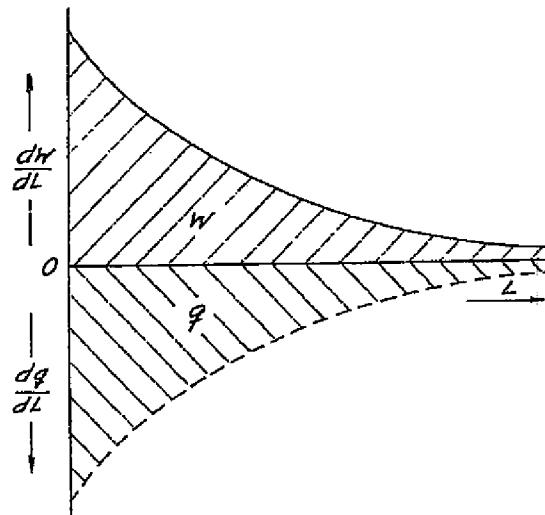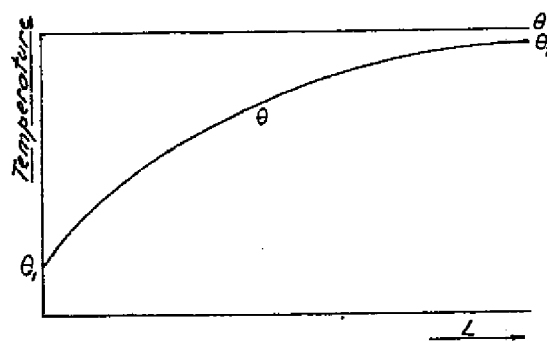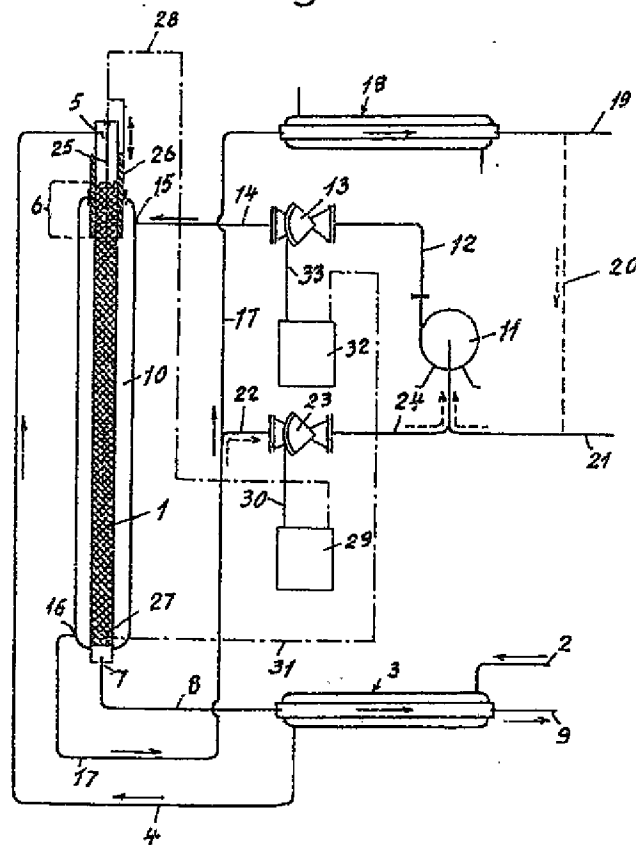SHEETS 1 & 2

Fig.2.

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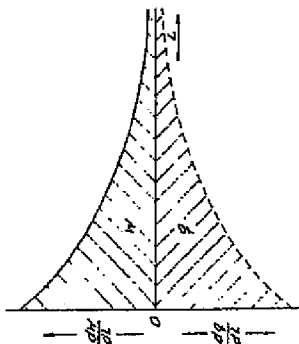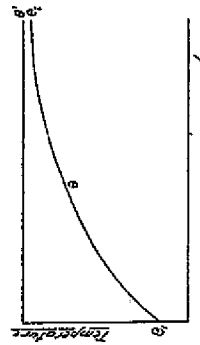the Original on a reduced scale.
SHEETS 1 & 2

Fig.2.

Fig.1a.

Fig.1b.

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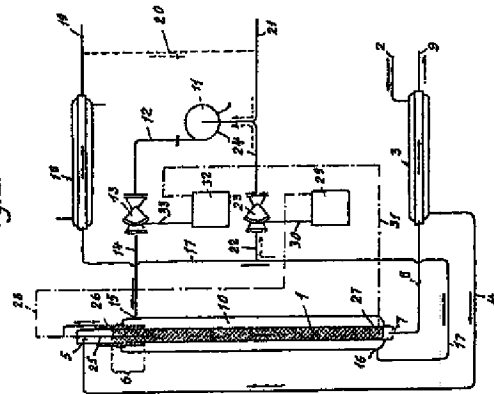the Original on a reduced scale.
SHEET 3

Fig.3.